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(71) Applicant: **IMPERIAL CHEMICAL INDUSTRIES  
PLC**  
Imperial Chemical House, Millbank  
London SW1P 3JF(GB)

(72) Inventor: **Colquhoun, Howard Matthew**  
8 Grove Park  
Knutsford, Cheshire WA16 8QA(GB)  
Inventor: **Taylor, Thomas Mark Cavell**  
29 Heathfields Close  
Chester CH2 2AT(GB)

(74) Representative: **Thomas, Ieuan et al**  
Imperial Chemical Industries PLC, Legal  
Department: Patents, PO Box 6, Bessmer  
Road  
Welwyn Garden City, Herts, AL7 1HD(GB)

(54) **Membranes.**

(57) An asymmetric membrane which comprises an at least partially crystalline aromatic ether ketone polymer may be prepared by contacting a solution of the polymer in a strong acid in a suitable shape with a non-solvent for the polymer.

**EP 0 382 356 A2**

## MEMBRANES

This invention relates to membranes, particularly asymmetric membranes suitable for use in filtration and the preparation and use thereof.

By "asymmetric membrane" we mean a membrane (a) which comprises, on the side adjacent the solution to be filtered, a skin of thickness 0.05-2.0  $\mu\text{m}$  supported on a substrate of thickness 30-250  $\mu\text{m}$ ; (b) in which both the skin and the substrate comprise the same polymer; and (c) in which the pore sizes of the substrate is greater than the pore sizes of the skin. It is known that such membranes may be used in ultrafiltration and microfiltration and, when suitably coated with hydrophilic polymer, in reverse osmosis.

Asymmetric ultrafiltration and microfiltration membranes can be prepared by the well established phase-inversion process developed by Loeb and Sourirajan (Adv. Chem. Ser. 38, 117, 1963). In that process a selected polymer is dissolved in a solvent and subsequently precipitated by addition of a non-solvent under controlled conditions. Polymers that have been used include cellulose acetate, polyimides, polyvinylidene fluoride, polysulphones, amorphous sulphonated polyetheretherketone, and polyamides. The solvents used include acetone, dimethylsulphoxide, dimethylformamide, dimethylacetamide, N-methylpyrrolidinone, concentrated sulphuric acid, and aqueous hydrochloric acid.

For such membranes, it is known that the size and density of the membrane pores is dependent on the concentration of the polymer solution and on the presence therein of pore-forming additives, e.g. salts, sugars and low MW polyethylene glycols (H Strathmann in "Material Science of Synthetic Membranes", Lloyd, ACS 269, 1984).

Membranes prepared from the aforesaid polymers tend to suffer from one or more of the following disadvantages. For example, they can be used in a limited temperature range, e.g. 0-90°C; they are unable to withstand sterilisation by super-heated steam; they have a limited chemical stability to, for example, acids, bases and oxidising agents; they are soluble in, or swellable by, organic solvents, e.g. at room or elevated temperature.

We have now prepared asymmetric membranes which overcome many of the aforesaid disadvantages. Such membranes may have (I) a pore size which allows their use in ultrafiltration or (II) a pore size which allows their use in microfiltration. Where the asymmetric membrane is suitable for ultrafiltration it may be used as the porous substrate of composite membranes for use in gas separation, pervaporation and reverse osmosis membranes.

According to a first aspect of the present invention there is provided an asymmetric membrane comprising an at least partially crystalline aromatic ether ketone polymer.

By partially crystalline we mean that the level of crystallinity is at least about 10%, preferably at least 15%, more preferably at least 20% and particularly more preferably at least 30% weight fraction. Such crystallinity is measured by wide angle X-ray diffraction as described by Blundell and Osborn (Polymer 24, 953, 1983).

By "aromatic ether ketone polymer" we mean a polymer in which inter-ring ether linkages and interring ketone linkages together provide at least a major portion of the linkages between aromatic units in the polymer backbone. We do not exclude the possibility that a portion of the aromatic rings may be replaced by a heterocyclic ring, eg pyridine.

As examples of aromatic ether ketone polymers of which the membrane according to the present invention may be comprised may be mentioned inter alia polymers and copolymers illustrated in the drawings appended hereto.

In the drawings:

Figure 1 illustrates polymer chains in which the aromatic rings are joined by ether or ketone bonds (I-VI);

Figure 2 illustrates polymer chains in which a portion of the aromatic rings are joined by direct links (VII-IX) or are bicyclic rings (X);

Figure 3 illustrates copolymer units bearing intercyclic  $-\text{SO}_2-$  bonds (XI-XII);

Figure 4 illustrates certain copolymers containing ketone and ether links (XV) or in addition, a mixture of biphenyl and sulphone linkages (XIV and XVI);

Figure 5 illustrates a typical wide angle X-ray diffraction curve for a membrane according to the present invention; and

Figure 6 illustrates a scanning electron micrograph of a cross-section through a typical membrane according to the present invention.

Each such polymer-type is hereinafter referred to for convenience by the trivial name appended thereto in the drawings.

It will be appreciated that in Figures 1-4,  
 E represents an ether linkage;  
 K represents a ketone linkage;  
 D represents a direct linkage;  
 5 m represents a meta substituted aromatic ring;  
 N represents a naphthalene ring; and  
 S represents a sulphone linkage except where it is used as a prefix to the polymer trivial name where it represents "sulphonated".

We do not exclude the possibility that at least a portion of the ether linkages in the polymers illustrated  
 10 in Figures 1-4 may be replaced by thioether linkages.

The preparation of polymers illustrated in certain Figures of the drawings are described in inter alia  
 Journal Macromolecular Science, Review of Macromolecular Chem. Phys., (27 (2), 313-341, 1987 (General  
 Formulae I-VIII); European Patent Specification No 0,323,076 (General Formula IX); Polymer 1984, vol 25  
 (August), 1151 (General Formula X); EPA 0,194,062 (General Formula XIV) and co-pending British Patent  
 15 Application BPA 89, 10549 (General Formula XVI).

Whereas the polymer is preferably a homopolymer, e.g. PEEK or PEK, we do not exclude the  
 possibility that it may be a copolymer e.g. PEEK/PEK, PEEK/PES, PEK/PES, PEEK/PEES, wherein the  
 copolymer units are represented by the General Formulae XI-XII in the drawings appended hereto.

It will be appreciated that where a copolymer is used the nature and molar percentage of the  
 20 "comonomer" will be chosen such that it does not unduly decrease the crystallinity of the polyetherketone  
 component of the copolymer and that the inter-aromatic links therein are non-hydrolysable under the  
 conditions of preparation and expected use of the membrane. As examples of comonomer units maybe  
 mentioned inter alia aromatic sulphones, sulphides, and biaryls.

We do not exclude the possibility that the membrane may be formed from a mixture of polymers, e.g.  
 25 PEEK/PEK or PEK/PES.

We have now found surprisingly that the membrane of the present invention may be prepared by  
 precipitation in a suitable form or shape, from a solution of the polymer in a strong acid by contacting the  
 solution with a non-solvent for the polymer. As examples of such suitable forms or shapes may be  
 mentioned inter alia tubular, capillary or sheet.

According to a second aspect of the present invention there is provided a process for the preparation of  
 30 a membrane according to the first aspect of the present invention which process comprises at least the step  
 of shaping a solution of an aromatic ether ketone polymer in a strong acid into the desired shape and then  
 contacting it with a non-solvent for the polymer such that the membrane of a suitable form, shape and size  
 is precipitated.

In the process according to the present invention, the strong acid is a substantially non-sulphonating  
 35 reagent towards the aromatic ether ketone polymer. For example, where the aromatic ether ketone polymer  
 is PEEK the strong acid is typically methanesulphonic acid.

The solution is formed by dissolving the polymer, typically in particulate form, in the strong acid under  
 an inert atmosphere, at a temperature and timespan sufficient to completely dissolve the polymer. At this  
 40 stage a pore-forming agent may be, added for example an inorganic salt; a soluble amorphous organic  
 polymer, e.g. sulphonated polyetherethersulphone (XIII); or a low molecular weight organic compound, eg  
 acetophenone.

A sheet membrane is typically formed by casting the polymer solution as a thin liquid film, typically of  
 thickness between 20 and 500  $\mu\text{m}$ , onto a suitable substrate which is not attacked by the strong acid  
 45 solution. The membrane can be supported by a porous fabric e.g. of polyethylene, polypropylene, PEEK,  
 polyester, PTFE or carbon fibre. Alternatively, the membrane can be unsupported in which case the film  
 would be cast onto a plane non-porous surface, e.g. a band of stainless steel, PTFE or polypropylene or a  
 sheet of glass.

The polymer is then precipitated by treating the shaped solution with non-solvent under suitable  
 50 conditions, e.g. it may be immersed in non-solvent liquid in a gelation bath, or non-solvent vapour may be  
 allowed or caused to diffuse into it.

A capillary membrane may be formed by extruding the polymer solution through the outer annulus of a  
 coaxial die. Through the inner nozzle there is a flow of suitable fluid, e.g. an inert gas or liquid, which is a  
 non-solvent for the polymer.

The precipitated membrane is then allowed to remain in contact with the non-solvent for a time  
 55 sufficient to allow substantially complete gelation of the polymer, then removed from the non-solvent.

The residual strong acid/non-solvent is removed from the membrane by treatment with an aqueous  
 medium, e.g. water or an aqueous base, at an appropriate temperature, e.g. between room temperature and

the boiling point of water. Often further treatment with an organic medium, e.g. acetone, is necessary to reduce the amount of acid present in the membrane further.

The membrane may be subjected to a treatment to enhance crystallinity. As examples of such treatment may be mentioned *inter alia* heating dry above the T<sub>g</sub> of the polymer; treatment with a polar aprotic solvent, e.g. acetone, dimethylformamide (DMF) or dimethylacetamide (DMA). Where DMF or DMA is used in such treatments it is later removed by a suitable further treatment, e.g. by washing with acetone.

Preferably the strong acid is water-free although we do not exclude the possibility that it may contain a small amount, for example up to about 10%, of water.

It will be appreciated that the strong acid will be chosen in the light of the structure of the polymer. For example, it should not react chemically with the polymer to unduly reduce the crystallinity thereof. For example, whereas 98% sulphuric acid reacts unduly with polyetheretherketone (PEEK) and should not be used therewith, it can advantageously be used with polyetherketone (PEK) in the process according to the present invention. The strong acid should be a good solvent for the polymer and, after membrane formation, should be readily extractable therefrom.

We do not exclude the possibility that the strong acid may be a mixture of acids, eg sulphuric acid and acetic acid. It will be appreciated that where one of the acids in the mixture is a non-solvent for the polymer the concentration thereof will be insufficient to inhibit solvation of the polymer in the mixture. For example, where the strong acid is a mixture of sulphuric acid and acetic acid the concentration of acetic acid is typically less than 15% w/w.

As examples of strong acids for use in the process of the present invention may be mentioned *inter alia* sulphuric acid, liquid hydrogen fluoride, methane sulphonc acid, fluoromethane sulphonc acid, and di- and tri-fluoromethane sulphonc acid.

It will be appreciated that the skilled man will take appropriate precautions where he uses any of the above acids.

We do not exclude the possibility that a further solvent may be used in combination with the strong acid, with the proviso that it does not unduly impair the solvent power of the strong acid, or react with the strong acid or unduly react with the polymer in the presence of the strong acid.

As typical examples of such further solvents may be mentioned *inter alia* liquid sulphur dioxide, 1,2,4-trichlorobenzene, 1,2-dichloroethane, dichloromethane, dichloroacetic acid and trifluoroacetic acid.

We have found that the presence in the strong acid of a small amount, typically less than 10%, of a non-solvent, for example water or an organic liquid, e.g. acetophenone, often impairs the solvency slightly and has the advantage that the gelation time for membrane formation is reduced allowing a higher rate of membrane production and may increase the porosity of the membrane or otherwise modify its structure.

Typically the concentration of the polymer in the strong acid in the process according to the present invention is between 5 and 50% w/w.

The non-solvent used in the process of the present invention may be a single component or a mixture. As examples of such non-solvents may be mentioned *inter alia* acetic acid, dilute sulphuric acid, water, methanol, ethanol. Dilute aqueous media, e.g. solutions of inorganic salts or bases may be used. It will be appreciated that such solutions may enhance the porosity of the membrane.

Electron microscopy has revealed that the membranes prepared by the process of the present invention have typical microporous structures, e.g. honeycomb (i.e. cellular and sponge-like) or extended finger-pore.

A scanning electron micrograph (1100 X magnification) of the cross section through a typical membrane according to the present invention prepared in Example 14, is shown in Figure 6 in which an asymmetric membrane with a honeycomb structure containing finger pores can be clearly seen.

It is well known that the honeycomb structure tends to be mechanically stronger than the extended finger-pore structure ("Synthetic Polymer Membranes", R E Kesting, John Wiley, 1985, pp. 282). It appears that, at least in part, the structure is determined by the interaction of the solvent/non-solvent combination with the polymer and each other.

The invention is further illustrated by reference to Figure 5 of the drawings appended hereto which shows, by way of example only, a typical wide-angle X-ray diffraction curve for an aromatic ether ketone polymer of which the asymmetric membrane is comprised. Figure 5 is more fully described hereinafter in relation to Examples 51-52.

The invention is further illustrated by reference to the following Examples.

#### Examples 1-4

These Examples illustrate asymmetric membranes according to the present invention prepared from a polyetherketone.

Polyetherketone (ICI, Victrex (RTM) PEK, having a melt viscosity of  $0.39 \text{ kNs/m}^2$  at  $1000 \text{ s}^{-1}$  at  $400^\circ \text{C}$ ; 10 g) was dissolved in 98% sulphuric acid at  $25^\circ \text{C}$  overnight under a dry atmosphere. After 12 hours a dark red 11% w/w solution was obtained.

From this solution a liquid film (200  $\mu\text{m}$  thick) was cast onto a dry glass plate.

In Examples 1 and 2, the film was immediately immersed in glacial acetic acid at  $5^\circ \text{C}$  to precipitate the membrane. After 1 hour the acetic acid solution was slowly exchanged for deionised water over 1 hour.

In Examples 3 and 4, the film was immediately immersed in 40% sulphuric acid to precipitate the membrane.

The white opaque membrane produced in Examples 1-4 was washed in boiling water and then in refluxing acetone to extract any residual sulphuric acid and/or acetic acid. Further crystallisation of the polymer was then effected (i) by heating the membrane in an oven at  $200^\circ \text{C}$  for 20 minutes (Examples 1 and 3) or (ii) by treatment with refluxing DMA for 30 minutes, washing in boiling acetone and drying at room temperature (Examples 2 and 4).

#### Examples 5-6

These Examples illustrate asymmetric membranes according to the present invention prepared from a polyetheretherketone polymer.

The procedure of Example 1 was repeated except that polyetheretherketone (ICI Victrex (RTM) PEEK 450P; melt viscosity of  $0.425 \text{ kNs/m}^2$  at  $1000 \text{ sec}^{-1}$  at  $380^\circ \text{C}$ ) was used instead of polyetherketone and methanesulphonic acid or trifluoromethanesulphonic acid was used instead of 98% sulphuric acid.

#### Examples 7-10

These Examples illustrate the use of hydrofluoric acid as the strong acid solvent in the process according to the present invention.

In a 6 cm diameter wide-mouth polypropylene bottle, polyetheretherketone (ICI Victrex (RTM) PEEK 450P, as used in Examples 5 and 6; 20 g) was dissolved in anhydrous hydrofluoric acid (50 ml) at  $5^\circ \text{C}$  under a nitrogen atmosphere over 30 minutes. A further portion (5 ml) of hydrofluoric acid was then added to compensate for evaporation losses to give a solution concentration of approximately 30% weight/weight polymer. Flat sheets of 3 cm wide PTFE were coated with polymer solution by dipping the sheet into the polymer solution, allowing excess polymer to run off during 30 seconds under a saturated HF atmosphere and then placing the coated sheet immediately into a polythene beaker containing glacial acetic acid (500 ml; the gelation agent) where it remained for 30 minutes.

The precipitated membrane was immersed in 5% aqueous potassium carbonate solution at room temperature for 1 hour and then the solution was boiled for 2 hours, the membrane was washed with water and crystallised by heating in an oven at  $200^\circ \text{C}$  for 20 minutes.

In Examples 8-10, the procedure of Example 7 was repeated except that different non-solvents were used instead of glacial acetic acid as shown in Table 1.

TABLE 1

EXAMPLE NO.	GELATION NON-SOLVENT
7	acetic acid
8	ethanol
9	water
10	5% $\text{K}_2\text{CO}_3$ in water

Examples 11-23

These Examples illustrate flat membranes prepared from further polymers and/or prepared under various conditions.

- 5 A solution of the polymer in a strong acid was cast under the conditions of Example 1 into a non-solvent. The membrane was washed with water. In Examples 11 and 15 the membrane was further crystallised by treatment with boiling acetone for 2 hours. The specific conditions are shown Table 2.

CT's 24 and 25 are comparative tests with Berghof (DE 3321860)

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TABLE 2

EX. No.	POLYMER	SOLUTION STRENGTH (w/w)	SOLVENT	GELATION NON-SOLVENT	WASHING CONDITIONS (Boiling)
11	PEK	10%	98% H <sub>2</sub> SO <sub>4</sub>	90% AcOH	water
12	PEK	10%	98% H <sub>2</sub> SO <sub>4</sub> /AcOH(9/1)	75% AcOH	water
13	PEK	15%	95% H <sub>2</sub> SO <sub>4</sub>	75% AcOH	water
14	PEK	12%	95% H <sub>2</sub> SO <sub>4</sub>	80% AcOH/10% AcONa/10% water	water
15	PEK	12%	95% H <sub>2</sub> SO <sub>4</sub>	37.5% H <sub>2</sub> SO <sub>4</sub> /37.5% AcOH/25% water	water
16	PEK	12%	95% H <sub>2</sub> SO <sub>4</sub>	50% H <sub>2</sub> SO <sub>4</sub>	water
17	PEK	10%	95% H <sub>2</sub> SO <sub>4</sub>	8% NaHSO <sub>4</sub> /water	water
18	COPOL1, X = 0.4	10%	98% CF <sub>3</sub> SO <sub>3</sub> H	75% AcOH/8% AcONa/17% water	water
19	PEKK	10%	98% CF <sub>3</sub> SO <sub>3</sub> H/MeSO <sub>3</sub> H(19/1)	75% AcOH/8% AcONa/17% water	water
20	PEKK	10%	98% H <sub>2</sub> SO <sub>4</sub>	75% AcOH/8% AcONa/17% water	water
21	PEKEKK	10%	98% H <sub>2</sub> SO <sub>4</sub>	75% AcOH/8% AcONa/17% water	water
22	COPOL2, X = 0.05	10%	98% CF <sub>3</sub> SO <sub>3</sub> H	75% AcOH/8% AcONa/17% water	water
23	PEDEKmk	10%	CF <sub>3</sub> SO <sub>3</sub> H/MeSO <sub>3</sub> H(19/1)	75% AcOH/8% AcONa/17% water	water
CT24	PEEK	5%	96% H <sub>2</sub> SO <sub>4</sub>	water	water
CT25	PEEK	10%	96% H <sub>2</sub> SO <sub>4</sub>	water	water

CT24 and CT 25 are Comparative Tests

In CT 24, a 5% solution of polyetherketone (ICI Victrex 450-P PEEK) in 96% sulphuric acid was formed by stirring at room temperature for 18 hours, and was then coated onto a polyester backing cloth, [c.f. DE 3321860 Example 4] using a casting knife set to give a 200 $\mu$  cast film thickness. The membrane was coagulated in water for an hour and then washed in water, soaked for 24 hours in water, and washed again. On attempting to crystallise a sample of the membrane by heating it in dimethylformamide, the sulphonated polyetherketone was found to soften at about 80 °C and began to dissolve at about 120 °C.

In CT 25, a 10% solution of polyetherketone (ICI Victrex 550-P PEEK) in 96% sulphuric acid was formed by stirring at room temperature for 24 hours, and was then coated onto a glass plate using a casting knife set to give a 200 $\mu$  cast film thickness. The membrane was coagulated and washed as in Example 24, and was then dried and annealed at 200 °C for 30 minutes. Examination of the membrane by wide angle X-ray diffraction revealed the material to be essentially non-crystalline.

#### Examples 26-29

These Examples illustrate the use of pore-forming agents in the process according to the present invention.

A solution containing 12 wt% polyetherketone (PEK) or a copolymer (Example 29) and 5 wt%, or 4% (Example 28), pore-forming agent in 98% sulphuric acid was cast on to a glass plate as in Example 1, and then allowed to stand in air for 1 minute before coagulating in a bath of coagulant maintained at 2-4 °C. After 20 minutes, the precipitated membrane was washed with water and then soaked in water for 16 hours before washing with water. Residual pore-forming agent was removed by washing with acetone.

Details of the process are shown in Table 3.

TABLE 3

Example No.	Polymer	Additive Strength (w/w)	Polymer Strength (w/w)	Gelation Non-Solvent
26	PEK	5% AcPh	12%	A
27	PEK	5% AcPh	12%	B
28	PEK	4% SPEES	12%	A
29	COPOL3 X=0.125	5% BzPh	10%	B
A:75% acetic acid in water B:75% AcOH/8%NaOH/17% water AcPh = acetophenone BzPh = Benzophenone				

The chemical stability of the membranes prepared in Examples 26 and 27 was tested by filtering various solutions through the membrane at 6 bar pressure. The results are shown in Table 4.



TABLE 4

Membrane prepared in Example No	Solvent	Flux after 2 hours 1/m2h.bar	Flux after 4 hours 1/m2h.bar
27	acetone	91.4	84.9
27	toluene	61.4	59.1
27	n-methylpyrrolidone	19.1	22.9
27	33% aq. hydrochloric acid	11.94	*
27	30% aq. sodium hydroxide	14.33	11.94
26	1,1,1-trichloroethane	7.58	7.72
27	1,1,1-trichloroethane	7.2	7.3

\* failure of the PTFE lining in the Sartorius pressure cell stopped the test.

The membrane prepared in Example 27 was found to have a 90% rejection of particles greater than  $1\mu$  during the 1,1,1-trichloroethane test.

#### Example 30

This Example illustrates a membrane according to the present invention prepared from a blend of polyetherketones

A 10 wt% polymer solution, containing PEK (8%) and PEEK (2%) in 98% sulphuric acid was allowed to stand at room temperature for 20 days, and then cast onto a glass plate as described in Example 1 and coagulated in a gelation bath containing 75 wt% acetic acid, 17 wt% water, and 8 wt% sodium acetate, at 4°C. After 1 hour the precipitated membrane was washed with water and then soaked in water for 16 hours before washing again with water.

#### Examples 31-41

These Examples illustrate hollow fibre membranes according to the present invention.

#### General Procedure

A 35% w/w dark red solution of polyetherketone (PEK) (except Example 36 where COPOL3,  $X = 0.125$  was used instead of PEK) in 98% sulphuric acid prepared by dissolving the polymer (60gm; of melt viscosity  $0.19 \text{ kNs/m}^2$  at  $1000\text{s}^{-1}$  at  $400^\circ\text{C}$ ) in 98% sulphuric acid (340 gms) at  $25^\circ\text{C}$  was transferred to the reservoir of a spinning unit of the general type described in Kirk-Othmer "Encyclopedia of Chemical Technology", Third Edition, Volume 12, p497 et seq, John Wiley & Sons, New York. The solution was degassed several times and was extruded under pressure, eg 15-30 psi at  $4.6 \text{ cm}^3/\text{min}$  through a stainless steel tube-in-hole spinneret (hole diameter: 1.5mm; tube diameter: 0.55mm) into a bath (4-8cm) of cold water with an air gap of 7.0cm. Water was used as the internal gelating agent with a water injection rate of  $16.5 \text{ cm}^3/\text{min}$

The extrudate was wound onto a drum winder at  $6\text{m}/\text{min}$  to give a fibre which after extraction by boiling in water for about 2 hours and Soxhlet extraction with acetone over about 6 hours and drying, had an outer diameter of 1.15mm and wall thickness of 0.17mm. The gas permeation rate for nitrogen was then measured using a Sartorius SM 16223 membrane cell connected to a mass flow meter and pressure gauge.

The experiment was repeated using different polymer concentrations and different internal gelation non-solvents. The specific conditions and gas permeation results are shown in Table 5. Further results on certain membranes prepared in these Examples are shown in Tables 6 and 8.

In Example 35, the external surface of the capillary was etched with a gas plasma.

From Table 5 it can be seen (i) that there is a broad inverse correlation between the membrane permeability and polymer concentration in the spinning solution e.g. compare Examples 40, 38 and 31, (ii)

plasma etching of the membrane enhances permeability (compare Examples 35 and 40) and (iii) the gas permeation results reveal that the membranes have adequate permeability to be commercially useful in ultrafiltration.

TABLE 5

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EXAMPLE NO.	STRENGTH OF POLYMER SOLUTION (w/w)	INTERNAL GELATION NON-SOLVENT	PERMEATION RATE CONSTANT FOR N <sub>2</sub> , P×10 <sup>9</sup> (kmol s <sup>-1</sup> m <sup>-2</sup> Pa <sup>-1</sup> )
31	15	water	0.4
32	11	water	4.1
33	11	water	15.3
34	10	10% H <sub>2</sub> SO <sub>4</sub>	29.7
35	8	water	403
36	10	water	258
37	15	20% AcOH	3.1
38	12	water	38
39	10	20% H <sub>2</sub> SO <sub>4</sub>	30
40	8	water	330

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Example 41

This Example illustrates the preparation of a PEK membrane according to the present invention on a non-woven support.

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A 10% solution of polyetherketone (PEK) in 95% sulphuric acid was cast onto a non-woven polyethylene cloth using a casting knife with the gap set to 200μ. The membrane was coagulated by immersion in 90% aqueous acetic acid. After 1 hour the membrane was washed with water, allowed to soak in water for 16 hours, rinsed with water and then soaked in water for a further 6 hours before allowing it to dry in air.

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Example 42

This Example illustrates the capability of a membrane of the present invention to withstand steam sterilisation.

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A sample of the membrane prepared in Example 27 gave pure water flux of 23.6 litres/m<sup>2</sup>/hr at 6 bar. After steam-sterilisation at 121 °C for 2 hours in an autoclave, the pure water flux of a sample was 19.1 litres/m<sup>2</sup>/hr, increasing to 22.3 litres/m<sup>2</sup>/hr after a 7 hour flux test.

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Example 43

This Example illustrates a thin-film composite reverse osmosis membrane wherein a PEK ultra-filtration membrane according to the present invention provides the support membrane.

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A sample of the membrane prepared in Example 27 was soaked in 10% aqueous butane-1,4-diol at 60 °C for 10 minutes and then oven dried at 70 °C for 10 minutes. The membrane was then coated with a 5% solution of cellulose acetate (Eastman 4655, 39% acetyl) in chloroform using a brush-technique, and then oven dried at 70 °C for 5 minutes. The resulting membrane gave a salt rejection of 73.5% and a flux of 5.3 litres/m<sup>2</sup>/day when tested in reverse osmosis (crossflow at 0.8 litres/min, 40 bar pressure) using a solution containing 2000ppm of sodium chloride.

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Example 44

This Example illustrates a thin film composite membrane for gas separation wherein a PEK UF

membrane according to the present invention provides the support membrane.

A sample of the membrane prepared in Example 27 was brush coated with liquid silicone rubber (Dow Corning 3140 RTV), and the silicone cured for 16 hours at room temperature. The membrane was tested in a gas permeability cell. With air as the test gas, the permeation rate constants for oxygen and nitrogen (kMol/m<sup>2</sup>/s/Pa) were found to be  $3.35 \times 10^{-14}$  and  $2.09 \times 10^{-14}$  respectively, giving a separation factor for the two gases of 1.69.

#### Example 45

This Example illustrates the preparation of a thin-film composite pervaporation membrane wherein a PEK ultra-filtration membrane according to the present invention provides the support membrane.

A sample of the membrane prepared in Example 27 was soaked in 10% aqueous butane-1,4-diol at 60°C for 10 minutes and then oven dried at 70°C for 10 minutes. The membrane was then brush-coated with a 10% solution of fluorosilicone rubber (Dow Corning Silastic 730) in acetone, and dried at 70°C for 5 minutes. Pervaporation through this membrane of a 40/60 (v/v) mixture of ethanol and water (2 bar feed pressure;  $2 \times 10^{-2}$  bar permeate pressure) gave a separation factor (ethanol/water) of 5.7, at a flux of 1.14 kg/m<sup>2</sup>/day.

#### Examples 46-66

These Examples illustrate the separating limits of certain membranes prepared in the above Examples.

A sample of each membrane was separately mounted in a Sartorius SM16223 cell. It was washed with 18% acetone in water (5 ml), deionised 18MΩ water (50 ml), and 0.85% saline (5 ml) solution before being subjected to the following tests.

The flux and rejection of the membranes against the following substrates were determined:-  
BSA: 0.1% solution of Bovine serum albumin (molecular weight 67,000) in 0.85% saline;

Cytochrome C: molecular weight 12,327;

γ-Globulin: molecular weight 150,000;

Vitamin B12: molecular weight 1,355.

In Example 47, a further sample of the membrane prepared in Example 5 was mounted in a Sartorius SM16223 cell. It was washed with 18% acetone in water (5 ml) and deionised 18MΩ water (50 ml). The flux and rejection of a 0.1% aqueous suspension of 0.05 μm polystyrene latex demonstrate the effectiveness of this membrane as a microfiltration membrane.

In Example 48, the microfiltration membrane from Example 47 was washed with water to remove loose latex from the membrane surface and then used to filter successively 70% aqueous nitric acid at 2 bar over 15 hours, pure water for 2 minutes and then 40% aqueous H<sub>2</sub>SO<sub>4</sub> for 2 hours. The resulting membrane was found to have a flux of 200 l/m<sup>2</sup>/h at 2 bar and a 95% rejection of a 0.1% aqueous suspension of 0.05 μm polystyrene latex.

The results obtained in Examples 46-65 are shown in Table 6.

TABLE 6

Example No.	Membrane prepared in Example No	Test Solution litre/m <sup>2</sup> /hour/bar	Test Flux	Rejection
46	5	BSA	65	2.0%
47	5	0.05 $\mu$ m latex	150	99.95%
48	5 then HNO <sub>3</sub> &H <sub>2</sub> SO <sub>4</sub>	0.05 $\mu$ m latex	100	95.0%
49	4	BSA	20	99.0%
50	42	Cytochrome C	1.5	10.7%
51	42	BSA	0.7	33.3%
52	42	$\gamma$ globulin	0.2	99.9%
53	26	Vitamin B12	6.7	0.0%
54	26	Cytochrome C	5.7	14.7%
55	26	BSA	5.3	98.0%
56	26	$\gamma$ globulin	0.8	99.9%
57	27	Vitamin B12	15.9	0.0%
58	27	Cytochrome C	11.9	0.0%
59	27	BSA	8.2	94.7%
60	27	$\gamma$ globulin	5.5	99.9%
61	17	Vitamin B12	0.4	47.1%
62	17	Cytochrome C	0.2	99.7%
63	17	BSA	0.05	99.9%
64	17	$\gamma$ globulin	0.05	99.9%
65	40	Cytochrome C	11.4	30.9%
66	40	BSA	10.2	97.8%

Example 67-68

These Examples illustrate the crystallinity of membranes according to the present invention.

The extent of crystallinity of a PEEK membrane was determined by the following method. Wide-angle X-ray diffraction was carried out on a Philips PW1050 vertical goniometer fitted with a PW1130 X-ray generator at 50 kilovolts and 40 milli-amps long sine focussed copper X-ray tube, and operated in reflection mode, using a proportional counter detector with a graphite monochromator.

The sample was mounted on a single silicon crystal cut so as to give no silicon reflections.

The sample was scanned from 5° to 45° in two theta, taking 20 points per degree and counting for 5 seconds per point. The data was processed on a DEC PDP1123+ computer.

The level of crystallinity in the membrane sample was estimated according to the method of Blundell and Osborn, Polymer 24, 953, 1983. Figure 5 illustrates a typical wide-angle X-ray diffraction curve for a membrane prepared and crystallised as described in Example 6. Estimates of crystallinity were obtained by drawing a straight baseline between  $2\theta = 10^\circ$  and  $35^\circ$ , and then fitting a scaled amorphous curve under the diffraction peaks in the manner indicated by the broken line in Figure 5. The ratio of the areas of the crystalline peaks to the total area was taken as a weight fraction for the crystallinity.

The crystallinity of a sample of PEK membrane prepared and heated in DMA at reflux as described in Example 4 was measured as above.

The results are shown in Table 7.

TABLE 7

Example No	Membrane prepared in Example No.	% crystallinity w/w
67	6	20
68	4	31
CT	CT24	0
CT	CT25	0
CT: Comparative Test using Berghof membrane.		

Example 69

This Example illustrates certain fluxes which are obtainable from asymmetric membranes according to the present invention.

Pure water and acetone fluxes, were determined using a Sartorius SM 16223 membrane cell.

The results are shown in Table 8 from which it can be seen that (i) there is typically an increase in acetone flux as polymer concentration in the strong acid solution is decreased (compare membranes prepared in Examples 40 and 38) and (ii) that the liquid permeabilities of the membranes are in a commercially useful range for ultrafiltration, eg membranes prepared in Examples 20 and 23 and microfiltration, eg membrane prepared in Example 5.

TABLE 8

MEMBRANE prepared in Example No	PURE WATER FLUX litres/m <sup>2</sup> /hour		ACETONE FLUX litres/m <sup>2</sup> /hour	
	2 bar	6 bar	2 bar	6 bar
5	3000.0	-	-	-
4		140 at 5 bar	-	-
11			-	14.3
42	13.8	18.0	82.5	-
12		0.3	-	10:1
13		0.25		2.0
14	12.7	20.5		50.3
15		0.7		4.0
16		0.7		4.2
26	51.0	143.3		191.1
28	-			1.0
20	114.7			-
27	43.4			103.5
17	2.65			-
18	10.0			-
19	76.4			-
22	143.3			-
23	233.6			-
20		1.6		-
21		0.5		-
29		3.7		-
30	16.0			-
40	54.6		66.9	110
38	-		34.4	-
36	117		-	-

## Claims

1. An asymmetric membrane comprising an at least partially crystalline aromatic ether ketone polymer.
2. An asymmetric membrane as claimed in Claim 1 wherein the polymer comprises PEEK, PEK, PEKK, PEKEKK, PEEKK, PEEKEK, PEDK, PEDEK, PEDEKMK, PEKEKNK, COPOL 1 or COPOL 2 or a copolymer thereof.
3. An asymmetric membrane as claimed in Claim 1 wherein the polymer comprises a homo- or co-polymer of any one of PEEK, PEK, PEKK or PEEKK.
4. A composite membrane wherein at least one layer thereof is provided by an asymmetric membrane as claimed in any one of Claims 1 to 3.
5. An asymmetric membrane as claimed in any one of Claims 1-3 for use in gas separation, pervaporation, ultrafiltration or microfiltration.
6. A composite membrane as claimed in Claim 4 for use in gas separation, reverse osmosis, pervaporation ultrafiltration or microfiltration.
7. A method for the preparation of a membrane which method comprises a least the steps of
  - (A) shaping a solution of an aromatic ether ketone polymer in a strong acid into the desired shape, which acid substantially is non-sulphonating to the polymer;
  - (B) contacting the shaped solution with a non-solvent for the polymer under suitable conditions such that a membrane in a suitable form, shape, size and porosity is precipitated; and
  - (C) removing the membrane from the strong acid/non-solvent mixture.
8. A method for the preparation of a membrane as claimed in Claim 1 which method comprises a least

the steps of

(A) shaping a solution of an aromatic ether ketone polymer in a strong acid into the desired shape, which acid substantially is non-sulphonating to the polymer;

(B) contacting the shaped solution with a non-solvent for the polymer under suitable conditions such that a membrane in a suitable form, shape, size and porosity is precipitated; and

(C) removing the membrane from the strong acid/non-solvent mixture.

9. A method as claimed in Claims 7 or 8 wherein the strong acid is substantially water-free.

10. A method as claimed in any one of Claims 7-9 wherein the concentration of the polymer in the strong acid is between 5 and 50% w/w.

11. A method as claimed in Claim 7 or 8 comprising the further steps of treating the membrane with an aqueous medium.

12. A method as claimed in Claim 8 comprising the further step of treating the membrane to enhance its crystallinity.

13. A method as claimed in Claim 12 wherein the further step comprises treatment with a polar aprotic solvent.

14. A method as claimed in Claim 12 wherein the further step comprises heat treatment of the membrane after drying.

15. A method as claimed in Claim 7 or 8 wherein a pore-former is present in the solution of the polymer in the strong acid.

16. A method as claimed in Claim 15 wherein the pore-former is an organic material.

17. A method as claimed in Claim 7 or 8 wherein a pore-forming agent is present with the non-solvent in a gelation bath.

18. A process for gas separation, pervaporation, or reverse osmosis using a membrane as claimed in any one of Claims 1-6.

19. A micro-filtration or ultrafiltration process using a membrane as claimed in any one of Claims 1-6.

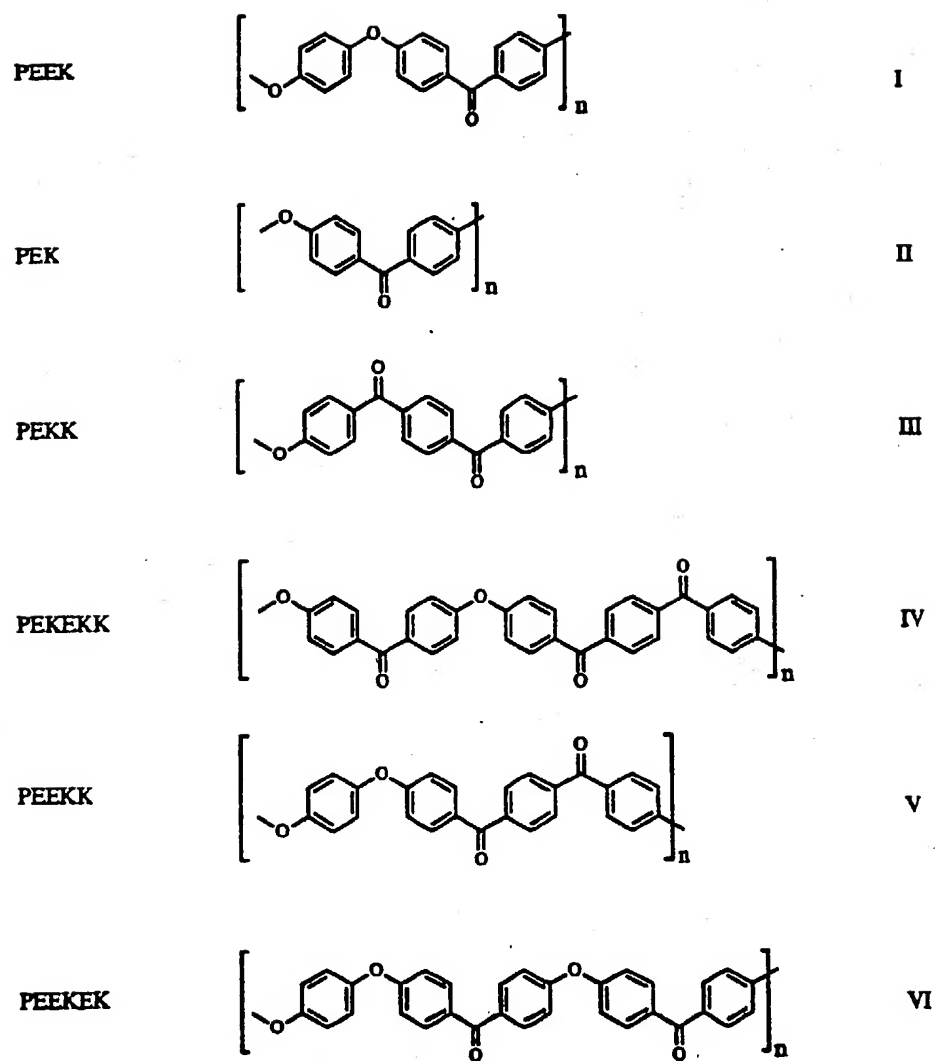
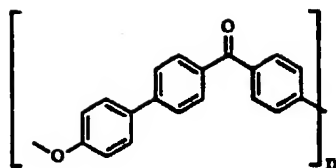


Figure 1

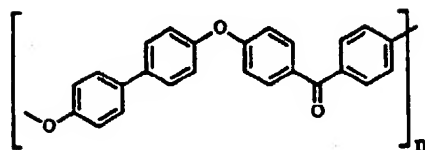


PEDK



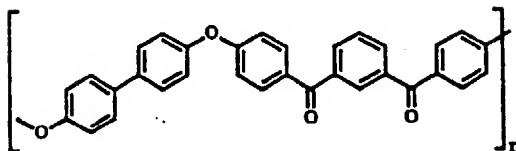
VII

PEDEK



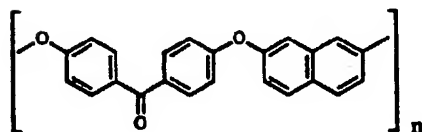
VIII

PEDEKmK



IX

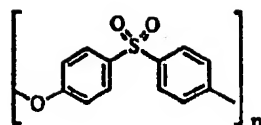
PEKEN



X

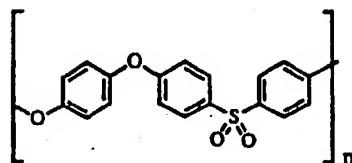
**Figure 2**

PES



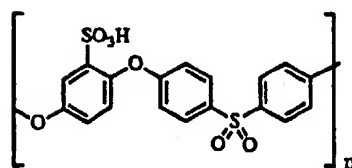
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PEES



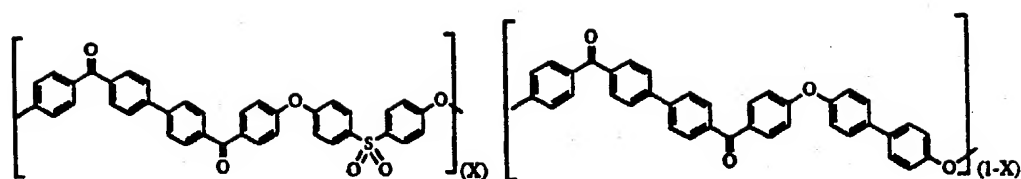
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SPEES

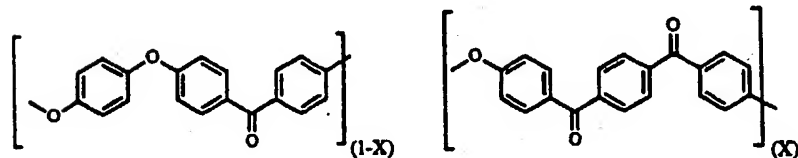


XIII

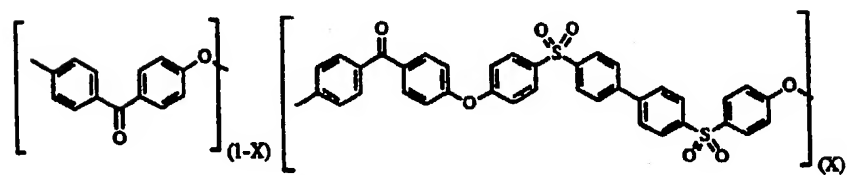
Figure 3



COPOL 1, (XIV)



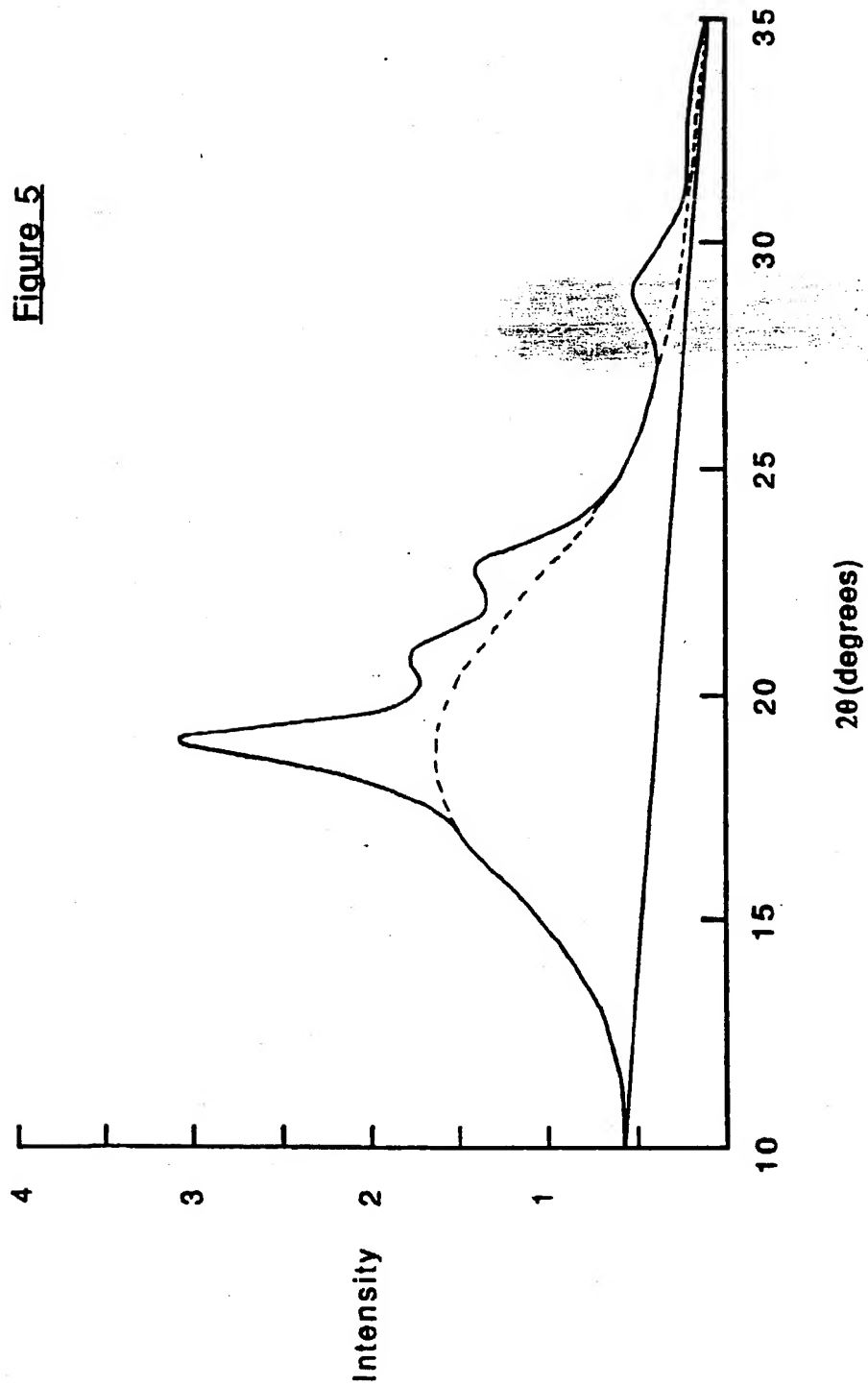
COPOL 2, (XV)



COPOL 3, (XVI)

**Figure 4**

**Figure 5**



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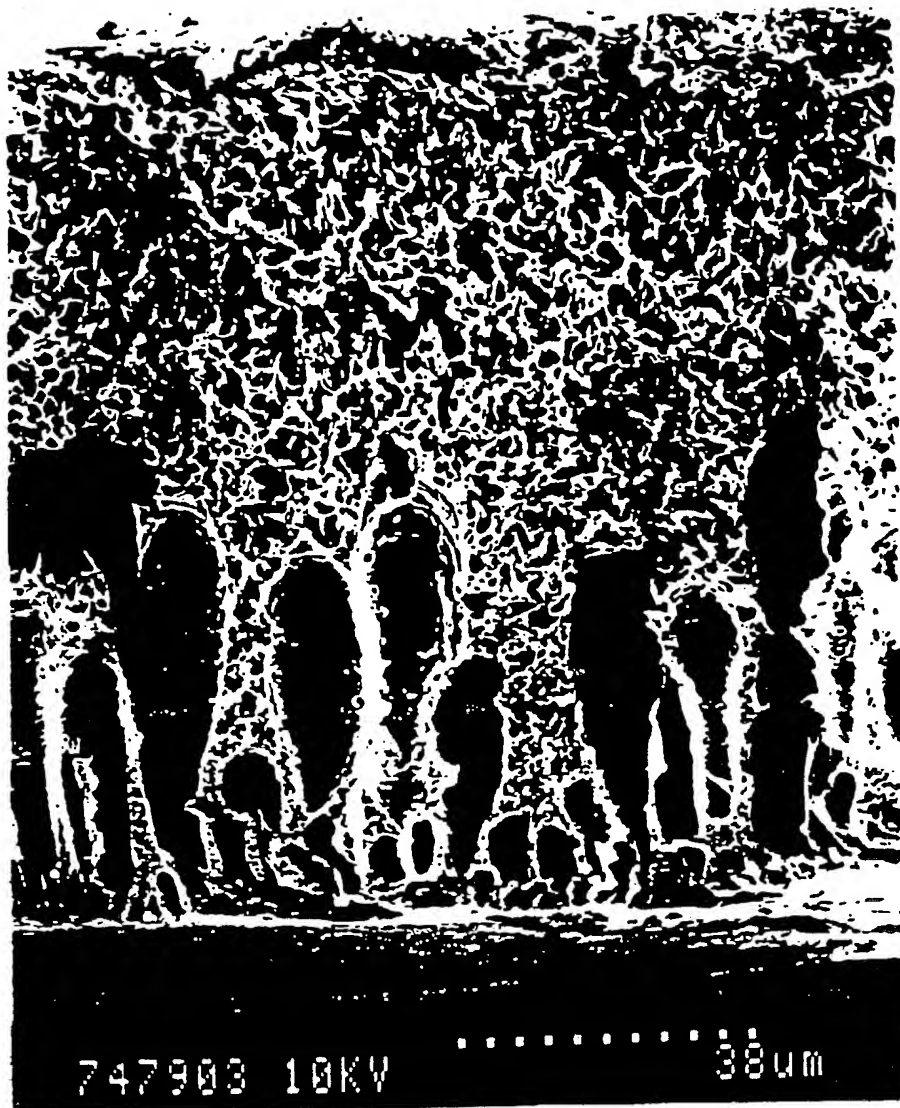


Figure 6

(19)



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(71) Applicant: IMPERIAL CHEMICAL INDUSTRIES  
PLC  
Imperial Chemical House, Millbank  
London SW1P 3JF(GB)

(72) Inventor: Colquhoun, Howard Matthew  
8 Grove Park  
Knutsford, Cheshire WA16 8QA(GB)  
Inventor: Taylor, Thomas Mark Cavell  
29 Heathfields Close  
Chester CH2 2AT(GB)

(74) Representative: Thomas, Ieuan et al  
Imperial Chemical Industries PLC, Legal  
Department: Patents, PO Box 6, Bessemer  
Road  
Welwyn Garden City, Herts, AL7 1HD(GB)

(54) **Membranes.**

(57) An asymmetric membrane which comprises an at least partially crystalline aromatic ether ketone polymer may be prepared by contacting a solution of the polymer in a strong acid in a suitable shape with a non-solvent for the polymer.

**EP 0 382 356 A3**



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# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 0570

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
E	EP-A-0 368 003 (DOW CHEM. CO.)(16-05-1990) * Abstract; claims 1-3,5,11,12,15-17; page 2, lines 24-35; page 3, lines 6-9; page 4, line 13 - page 5, line 4; examples 1-3,5,7-12 * ---	1-11,15 -19	B 01 D 71/52 B 01 D 67/00 B 01 D 61/00 B 01 D 53/22 C 08 J 9/28 // C 08 L 71/00
D,A	DE-A-3 321 860 (FORSCHUNGSINSTITUT BERGHOF) * Abstract; claim 1; examples 1,4,7 * ---	1-3,5,7 ,8,10, 18,19	
D,A	JOURNAL OF MACROMOL. SCIENCE - REVIEW OF MACROMOL. CHEM. PHYS., vol. C27, no. 2, 1987, pages 313-341, Marcel Dekker, Inc.; M.J. MULLINS et al.: "The synthesis and properties of poly[aromatic ketones]" * Page 314, lines 10-37; table 1; page 326, last paragraph - page 327, paragraph 1; table 4; page 337, lines 19-20; page 338, last paragraph * ---	1-3,7,8 ,12	
A	BRITISH POLYMER JOURNAL, vol. 17, no. 1, 1985, pages 4-10; X. JIN et al.: "A sulphonated poly(aryl ether ketone)" * Page 6, column 2, last paragraph - page 7, column 1, line 9 * ---	12,13	
A	EP-A-0 297 744 (I.C.I.) * Abstract; page 2, lines 4-5; page 3, line 56 - page 4, line 1; claim 9 * ---	1-3	
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A	EP-A-0 277 834 (HYDRANAUTICS) * Abstract; claims 1,5,6,8 * --- -/-	1,4,6, 18,19	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22-05-1990	Examiner HOORNAERT P.G.R.J.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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## EUROPEAN SEARCH REPORT

Page 2

Application Number

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A	CHEMICAL ABSTRACTS, vol. 110, no. 10, 6th March 1989, page 59, abstract no. 76905j, Columbus, Ohio, US; E. DRIOLI et al.: "Poly(ether ether ketone) ultrafiltration membranes", & MO KEXUE YU JISHU 1988, 8(2), 1-5 * Abstract * ---	1-3,5,7,8,18,19
A	CHEMICAL ABSTRACTS, vol. 110, no. 14, 3rd April 1989, page 20, abstract no. 115619r, Columbus, Ohio, US; Y. OOKOSHI et al.: "PEEK [poly(oxy-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylene)] gel from benzophenone solution", & SEN'I GAKKAISHI 1988, 44(12), 634-6 * Abstract * -----	1-3,7,8
The present search report has been drawn up for all claims		
Place of search THE HAGUE		Date of completion of the search 22-05-1990
Examiner HOORNAERT P.G.R.J.		
<b>TECHNICAL FIELDS SEARCHED (Int. Cl.5)</b>		
<b>CATEGORY OF CITED DOCUMENTS</b>		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		
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